J Mater Sci (2007) 42:7343–7347
DOI 10.1007/s10853-007-1584-z

Effect of inner oxygen on the interfacial layer formation for HfO_2 gate dielectric

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Received: 3 April 2006 / Accepted: 6 February 2007 / Published online: 15 May 2007

Abstract The interfacial layer (IL) formed at the HfO_2/Si interface was investigated by using Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Differently with the previous reports, it is concluded that the inner oxygen from bulk film predominates the oxidation process in interface region rather than the oxygen introduced from outer environment. First, from FT-IR, it is found that the formation of the IL strongly relies on the annealing temperature but does not obviously rely on the HfO_2 thickness and the annealing atmosphere. Second, the contradistinctive images of Hf/Si annealed in oxygen ambient and Hf/SiO_2 annealed in vacuum were investigated by TEM, which confirms the conclusion obtained from FT-IR data that the IL is formed not by a diffusion of the oxygen from the annealing atmosphere, but by a reaction within the interface region. Third, the Hf 4f, O 1s, and Si 2p core-level energy states of Hf/SiO_2 stack annealed in vacuum were investigated by XPS using two ways, one is investigating the samples annealed in vacuum for varied time and the other is investigating the fully oxidized sample in different depth. Based on the experiments, it is concluded that the inner oxygen from bulk films (HfO_2 or SiO_2) has greater influence on the IL formation comparing with the outer oxygen from environment.

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Introduction

According to the International Technology Roadmap for Semiconductors, the 70-nm node technology will require a gate dielectric with a capacitance effective thickness of ~1 nm, approaching the limit of SiO_2 thickness. Since scaling of SiO_2 below 1 nm is not acceptable due to tunneling leakage, and reliability concerns [1], high-*k* (permittivity) dielectric materials are needed to resolve these fundamental shortcomings. Among high-*k* materials, HfO_2 is attracting much attention due to its moderate permittivity (25), large band gap (5.7 eV) and compatible property with conventional CMOS process [2, 3]. However, the unacceptable interfacial layer (IL) is always formed in the interface of HfO_2/Si during deposition or post-annealing process [4]. The IL appears to be a critical issue for further scaling since it has a negative effect on the integrated *k* constant and injures the homogeneity of the overall film [5]. It is believed that the oxygen source responsible for interfacial oxidation is mainly from the outer environment, which reaches the interface region through surface and the high-*k* film [6, 7].

It is well known that the deposited HfO_2 films are always undergoing a post-anneal process in varied atmosphere for reducing impurities and defects in films and for increasing the dielectric constant by the structural melioration at a high temperature. Supposing it is true that the oxygen source responsible for interfacial oxidation is mainly from the outer ambient and this annealing oxidizes the interface between the HfO_2 and Si substrate, the post-deposition anneal (PDA) ambient should be controlled gingerly with the reduction of O_2. However, the source of the oxygen species that contribute to the IL formation has not undergone a precise confirmation as we known. The oxygen may come from the outer ambient that are used during the PDA, from physisorbed oxygen located within the grown HfO_2 film, or from a direct chemical reaction between the Si and the grown layer. Actually, it is an important issue when high-*k* material is in contact with silicon, which one predominates the oxidation process in interface region between the outer and the inter oxygen, because it determines what we should focus our energy on to control the IL growth. However, until now it is not clearly investigated and is accepted in subconscious sense that the outer ambient predominates the interfacial oxidation process.

In this letter, the growth and properties of the IL during post-deposition annealing were investigated. A standard reactive sputtering method was used to deposited high-*k* films followed by PDA treatments in vacuum or oxygen atmospheres. Afterwards, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the IL properties. From the resulting data, an explanation for the oxygen source for the IL growth is suggested. It is showed that the IL is formed not by a diffusion of the oxygen from the annealing atmosphere but by the reaction within the interface region. Meanwhile, considering that the interface with the substrate is usually protected by a high-*k* layer, the effect of the inter oxygen to interfacial oxidation is much greater than that of the oxygen from outer space.

Experimental

In this letter, we have not only prepared HfO_2 films on Si substrates, but also prepared Hf films both on overly etched Si substrates and on Si substrates covered by an O-rich SiO_2 layer in order to further understand the oxidation process in interface region. First, the *p*-Si substrates were all treated with a RCA cleaning followed by an overly etching process in HF (1%) resolution to expose the pure Si surface. Afterwards, for the sake of comparison, some of the substrates were annealed in O_2 ambient at 200 °C for 10 s to form a SiO_2 layer on the substrates. Finally, a standard reactive sputtering method was used to fabricate films.

HfO_2 films ranging from 10 to 100 nm in thickness were fabricated on Si substrates at 250 °C with 20 mTorr of oxygen followed by the annealing in vacuum or in O_2 environments under varied temperatures. To avoid the complexity caused by polycrystallinity, the anneal temperature is lower than 700 °C (from 300 to 700 °C).

The deposition of Hf films is operated at the same substrate temperature in an Ar ambient with a pressure of 10 mTorr. Some of the Hf films were deposited directly on a Si substrates (denoted as sample A), and some were deposited on the Si substrates treated by rapid thermal oxidation (denoted as sample B). After the deposition, the Hf/Si samples (sample A) were annealed in O_2 at 300 °C for 30 s and Hf/SiO_2 samples (sample B) were annealed in vacuum condition (~2×10^{-6} Torr) at 300 °C for 30 s.

All of the Hf films were analyzed by TEM. Sample B was investigated with a XPS system, using Mg Kα as the X-ray source. The thicknesses of both HfO_2 and Hf films were measured by using a UV-1280 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded by Bomem MB-100 spectrometer using the KBr wafer technique.

Results and discussion

Figure 1 shows the FT-IR absorption spectra of the 50-nm-thick HfO_2 samples annealed in vacuum for 10 min in the wave number range of 400–1,200 cm^{-1}. The annealing temperature is from 300 to 700 °C. In Fig. 1, the peaks of Si–O band have been signed with dash line. The peak of Si–O stretching mode is at 1,075 cm^{-1}, while the absorption peaks located at 800 and 464 cm^{-1} correspond to Si–O bending and rocking modes, respectively [8]. For as deposited samples, a thick SiO_2 formed in deposition process is always present, which is consistent with other reports [4, 5]. One can easily found that the Si–O peak intensity increases with the annealing temperature, especially for the typical Si–O peak at 1,075 cm^{-1}. As shown in Fig. 1, annealing in vacuum at 500 and 700 °C resulted in nearly diploid increase in the intensity of the 1,075 cm^{-1} peak (Si–O stretching mode). Similar increases were seen

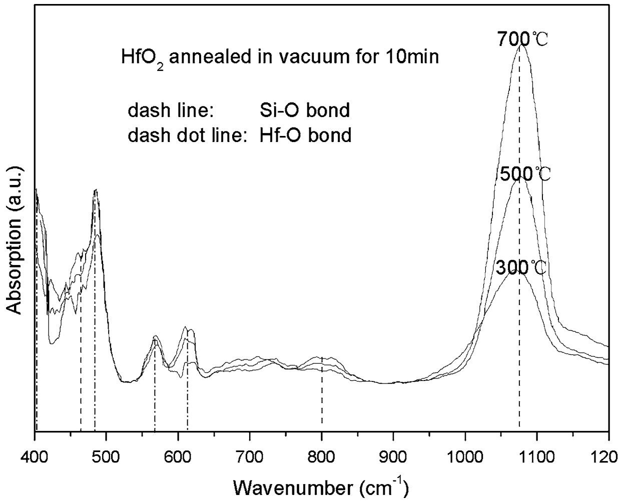


Fig. 1 FT-IR absorption spectra of the 50-nm-thick HfO_2 samples annealed in vacuum for 10 min in the wave number range of 400–1,200 cm^{-1}. The peaks signed with *dash line* correspond to Si–O band in different modes, while the peaks signed with *dash dot line* are related to Hf–O band

in the other absorption peaks of the Si–O bending and rocking modes.

Since the oxygen in the anneal atmosphere has to diffuse through the HfO_2 film to oxidize the Si substrate, if the outer oxygen does obviously affect the interfacial oxidation, the Si–O peak intensity in FT-IR must rely on the HfO_2 thickness. It is thus investigated using FT-IR for the HfO_2 films ranging 10–100 nm in thickness. Figure 2 is the relative peak intensity of the Si–O stretching mode (1,075 cm^{-1} in Fig. 1) after the baseline correction plotted against the HfO_2 thickness. The samples were as deposited and annealed at 700 °C in O_2 and vacuum ambient. From Fig. 2, it is noticed that the peak intensity did not rely on the HfO_2 thickness after annealing as well as before annealing. It should be noted that the constant trend was even spread to 100-nm-thick HfO_2 sample. Furthermore, the peak intensity is so close between O_2 annealing and vacuum annealing, which clearly imply that the interfacial SiO_2 formation is not controlled by a diffusion of oxygen in HfO_2 from the annealing atmosphere, and that the layer is formed by the reaction within the HfO_2/Si interface.

The only suspicion in the above conclusion is that HfO_2 layer may be responsible for the similarity of IL formation of samples annealed in O_2 ambient and in vacuum. Because if HfO_2 is overly oxidized, the physisorbed oxygen located within the grown HfO_2 film will indeed result in the similar IL formation, when samples annealed for a short time at varied ambient. To exclude the influence of HfO_2, we deposited a pure Hf metal layer onto Si surface (sample A) and onto a SiO_2 surface with Si substrate underlying (sample B). The former sample was annealed in O_2 while the latter was annealed in vacuum for comparison. Both anneals were lasted 30 s at 300 °C and the TEM imagine was shown in Fig. 3. Since sample A (the Hf/Si stack sample) was deposited on an overly etched Si substrate, thus, the interface of Hf/Si is somewhat fluctuant before anneal. After anneal in O_2 ambient for 30 s at 300 °C, at the top surface of the Hf film, a ~1.5 nm HfO_2 layer was formed due to the oxidation of the oxygen from outer environment. Since only a small fraction of Hf metal near top surface region is oxidized, from which the diffusion length of outer oxygen can be seen is limited (at least for our HfO_2 thickness). In addition, in Ref. [9], ‘‘Si oxidation at the HfO_2/Si interface is faster than that on the Si surface’’ was observed. This result strongly supports our conclusion, that is, the diffusion length of outer oxygen is limited and without the HfO_2’s catalyze, its reactive activity is lower than inner oxygen. Contrastively, in the interface of Hf/Si, there is not obvious formation of SiO_2 or HfO_2, and the thin interface layer region may be caused by the residual oxygen generated in sputtering process. The reason why we use ‘‘IL’’ after anneal instead of SiO_2 in Fig. 3 is because the interfacial layer should not only be in SiO_x form, which is confirmed by the Hf–Si bond and $HfSi_x$ void observation in Ref. [9]. Meanwhile, for the sake of comparison, sample B (Hf/SiO_2 stack) was deposited on a thin fully oxidized SiO_2 film. The sample was annealed in a vacuum at 300 °C for 30 s. It is obvious that the IL becomes much broader than the as deposited film even without the O_2 environment. According to the Ref. [9],

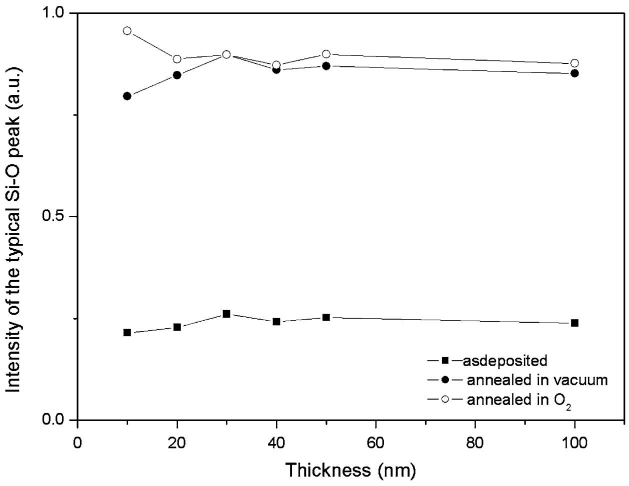


Fig. 2 Intensity of the typical Si–O absorbance peak (stretching mode at 1,075 cm^{-1}) versus the HfO_2 thickness. The samples were annealed at 700 °C for 10 min in O_2 atmosphere and in vacuum. For comparison, the as-deposited HfO_2 samples were also investigated and shown in the figure

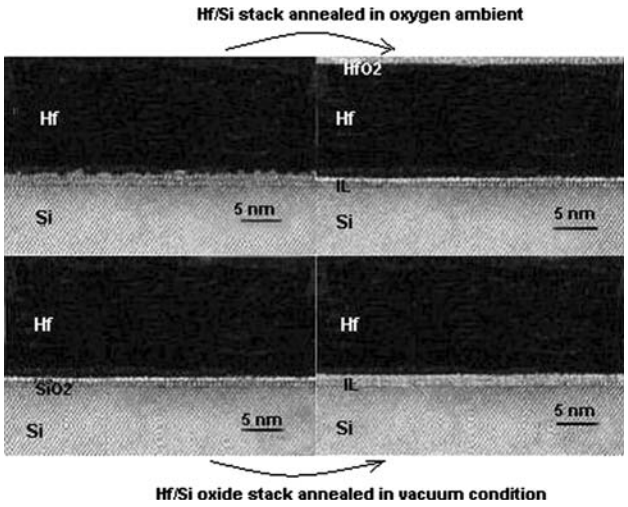


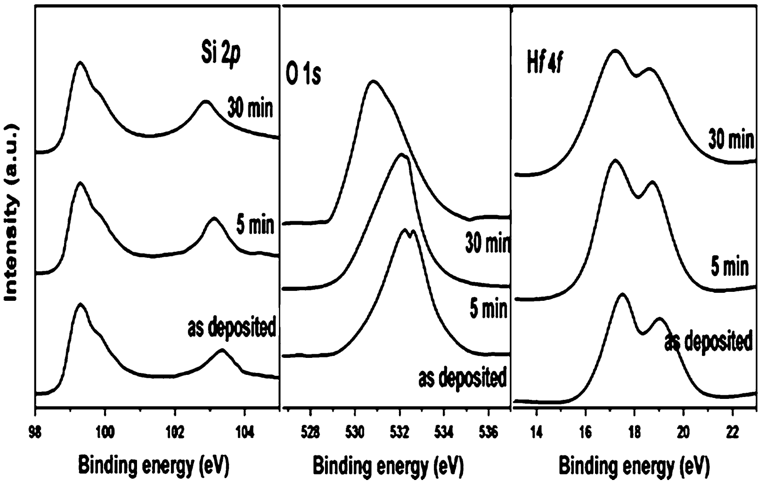
Fig. 3 The cross-sectional TEM images of sample A and B. the substrate in sample A is overly etched while the substrate in sample B is covered by a O-rich SiO_2 layer. Both samples were annealed at 300 °C for 30 s (sample A was annealed in O_2 ambient and sample B was annealed in vacuum)

the anneal condition (vacuum pressure and temperature) in our experiment is in the ''stable'' region for interfacial SiO_2 growth. It means that the vacuum anneal cannot influence the interfacial Si oxidation. Therefore, the obvious interface oxidation can only be ascribed to the inner oxygen. As for the original O-rich SiO_2 layer, it should be decomposed to SiO_x ($x < 2$) or even Si with a redox process [10].

To identify the result above, it is necessary to investigate the further oxidation of samples under longer-time annealing. As known, a SiO_2 layer is almost inevitable in the interface of the high-*k*/Si stack structure due to the oxidation of oxygen introduced in the deposition or thermal treatment process. Therefore, Hf/SiO_2 structure (sample B) annealed for varied time (0, 5 min and 30 min) in vacuum at 300 °C was investigated rather than Hf/Si structure (sample A) using XPS with 70° incident angle. As shown in Fig. 4, from Si 2p core-level spectra, it can be seen that the as deposited film has a peak at 103.4 eV, corresponding to the binding energy of SiO_2 [11]. It implies the presence of a SiO_2 layer on the substrate. However, after 5 min thermal annealing, the Si 2p peak shifted to 103.2 eV and with the anneal progress this peak shifted to even lower position to 102.9 eV for 30 min annealed film. The explanation about these peak shifts have been made by several reports [12, 13], giving the reason to the formation of additional SiO_2 or Hf silicate. The same trendy of peak shift can also be found from the O 1s and Hf 4f core-level spectra as shown in Fig. 4. It is noteworthy that on the high-energy side of the O 1s peak for as deposited and 5 min annealed samples, there is a small shoulder peak because Hf layer cannot be fully oxidized for insufficient anneals time. However, for 30 min annealed film the O 1s binding energy is fixed to 530.8 eV and the binding energies of Hf 4f 5/2 and Hf 4f 7/2 are fixed to 18.8 and 17.2 eV, respectively, corresponding to the formation of fully oxidized HfO_2. According to the experiments, longer time than 30 min cannot result obvious shift of the bond positions above. Since the anneal temperature is as low as 300 °C, and the saturated time of oxidation is only about 30 min, the diffusion efficiency of the inner oxygen is relatively high.

After all, the covering layer of IL region is always HfO_2 rather than Hf metal in the high-*k* stacks, thus the fully oxidized sample in Fig. 4 (i.e., 30 min annealed sample (its Hf/SiO_2 structure has been evolved to HfO_2/SiO_2 structure after anneal)) was further investigated. Via a XPS depth profile measurement at varying incident angles the transition of bonding states from interface to the top surface was investigated. As shown in Fig. 5, it can be seen that the intensity of Si–O peak is increased with the increase of incident angle, indicating that the oxidation is getting intense from surface to interface, which is easily understood because the oxidized source is from the O-rich SiO_2 rather than the outer environment. In addition, from the O 1s core-level spectra, shifts of the peak location can be also observed from the film surface to interface. At the film surface, the O 1s peak is located at 531.4 eV. However, with the angle increase to 90°, the peak shifted to 530.9 eV related to the interface. Therefore, we think that the upper layer of the film is somewhat in substoichiometric oxygen state, which may be explained by the exhaustion of the inner oxygen with the SiO_2 translated to SiO_x ($x < 2$) or Si. At the interface, as the absorbing oxygen atoms from the SiO_2 layer, the Hf-oxide was fully oxidized, as discussed in the previous sections. The shift tendency of the XPS spectra peaks indicates clearly the diffusion path from SiO_2 layer to the Hf film of the inner oxygen.

Fig. 4 Si 2p, O 1s, and Hf 4f core-level XPS spectra of sample B (Hf/SiO_2) annealed in vacuum condition at 300 °C for different time (0, 5, and 30 min)



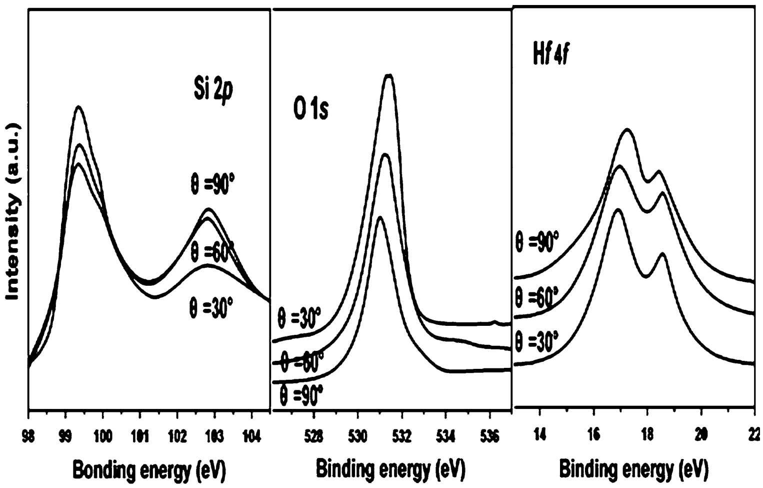


Fig. 5 XPS depth profile of sample B annealed in vacuum at 300 °C for 30 min. The incident angles are 30°, 60°, and 90°

Conclusion

In summary, the interfacial layer formed at the HfO_2/Si interface after the annealing in different atmospheres was investigated. FT-IR observations revealed that the IL formation relies neither on the HfO_2 thickness nor on the annealing atmosphere, but on the annealing temperature. The TEM images of the Hf thin films deposited on different substrates (with and without SiO_2-covered silicon) showed the domination of the inter oxygen species in the oxidation process. The XPS spectra of Hf films deposited on rich-O SiO_2 annealed for different time indicated that the Hf layer absorbs the oxygen in the SiO_2 layer to form oxidized metal oxide. Therefore, the IL formation is not mainly due to the oxygen diffusing through the bulk film from outer atmosphere during high-temperature heat treatments. Instead, it is mainly ascribed to the direct reaction within the interfacial region even under weak oxidation annealing.

References

1. Stathis JH, DiMaria DJ (1998) Tech Dig Int Electron Devices Meet 167
2. Wilk GD, Wallace RM, Anthony JM (2001) J Appl Phys 89:5243
3. Joo MS, Cho BJ, Yeo CC, Wu N, Yu H, Zhu C, Li MF, Kwong D-L, Balasubramanian N (2003) Jpn J Appl Phys 42:220
4. Emotoa T, Akimoto K, Yoshida Y, Ichimiya A, Nabatame T, Toriumi A (2005) Appl Surf Sci 244:55
5. Yamamoto K, Hayashi S, Kubota M, Niwa M (2002) Appl Phys Lett 81:2053
6. Cho M-H, Moon DW, Park SA, Kim YK, Jeong K, Kang SK, Ko D-H, Doh SJ, Lee JH, Lee I (2004) Appl Phys Lett 84:5243
7. Gougousi T, Parsons GN (2004) J Appl Phys 95:1391
8. Lau WS (1999) Infrared characterization for microelectronics. World Scientific, Singapore
9. Miyata N et al (2003) JJAP 42:L138
10. Wang SJ, Lim PC, Huan ACH, Liu CL, Chai JW, Chow SY, Pan JS, Li Q, Ong CK (2003) Appl Phys Lett 82:2047
11. Vincent BC (2000) Handbook of monochromatic XPS spectra. Wiley, New York
12. Jeon TS, White JM, Kwong DL (2001) Appl Phys Lett 78:368
13. Chang JP, Yin YS (2001) Appl Phys Lett 79:3824